RAMAN SPECTROSCOPY FOR THE FORENSIC EXAMINATION OF REACTIVELY DYED COTTON

by

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Certificate of Authorship and Originality

I certify that the work in this thesis has not been previously submitted for a degree nor has been submitted as part of the requirements for a degree except as fully acknowledged in the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

Jane Thomas

31st October 2005

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List of Abbreviations

AFP	Australian Federal Police
CI	Colour Index
CCD	Charged Coupled Device
CCTV	Closed Circuit Television
DP	Discriminatory Power
DNA	Deoxyribose Nucleic Acid
EFG	European Fibres Group
ENFSI	European Network of Forensic Science Institutes
ESI-MS	Electrospray Ionisation – Mass Spectrometry
ESI-MS/MS	Electrospray Ionisation – tandem Mass Spectrometry
FBI	Federal Bureau of Investigation
FPF	Fibre Plastic Fusion
FSS	Forensic Science Service
FTIR	Fourier Transform Infrared
GSR	Gun Shot Residue
IR	Infrared
MPFSL	Metropolitan Police Forensic Service Laboratory
MSP	Microspectrophotometry
mW	milli-watt
NIR	Near Infrared
nm	nano-meter
PCA	Principal Components Analysis
PCM	Plastic Coating Mark
Py-GC	Pyrolysis Gas Chromatography
SERRS	Surface Enhanced Resonance Raman Spectroscopy
SERS	Surface Enhanced Raman Spectroscopy
SWGMAT	Scientific Working Group for Materials
TLC	Thin Layer Chromatography
TWGFIBE	Technical Working Group for Fiber Examinations
UV	Ultraviolet
Vis-MSP	Visible Microspectrophotometry
XAM	Neutral medium improved white Gurr (Xylene based mountant)
ΔE	energy change
μm	micro-meter

Abstract

In the 21st Century, fibre examiners are faced with the constraints of time and money. Rapid advances in DNA technology has seen fibre evidence undervalued due to it being time consuming, costly and (when competing with DNA) perceived to be less discriminatory. However, DNA is not present in all cases and when present may require other evidence to interpret the circumstance/s. The only way forward for fibre examinations is through research that will address issues of time and money whilst increasing their evidentiary value by demonstrating reliability through improved statistical information.

Raman spectroscopy was investigated as it is a technique that is growing in popularity for the analysis of materials. It is quick, discriminatory, non-destructive and requires minimal sample preparation. The ability of Raman spectroscopy to discriminate black/grey and blue cotton fibres was investigated to determine how effective the technique would be for analysing this often undervalued fibre evidence.

Various parameters of Raman spectroscopy were investigated to determine the optimal conditions for the analysis of the samples selected. The major variable investigated was laser wavelength with the 785nm and 632.8nm lasers providing the best results. Results indicated that, at least, the major dye component could be identified using Raman spectroscopy.

The discriminatory power of the technique was then investigated for a sample set of 11 black/grey and blue cotton samples as well as a set of 91 black and blue cotton fibres of unknown dye types. This was then compared to the discriminatory power of microspectrophotometry (MSP) for the same sample sets as well as the discriminatory power of the combined techniques.

In analysis of both sample sets, Raman spectroscopy showed a lower discriminatory power than microspectrophotometry. However, combining the two techniques significantly increased the discriminatory power. Using chemometrics increased the discrimination provided by Raman spectroscopy indicating that chemometrics may be used as an aid for interpreting data.

Whilst the advantages of Raman spectroscopy were evident during these studies one major limitation of the technique was also highlighted. The problem of fluorescence has long been regarded as the major drawback to using Raman spectroscopy for fibre examinations. The problem was overcome in some instances by changing the laser wavelength but not all.

Even with the occurrence of fluorescence, it was shown that, for the sample sets investigated, Raman spectroscopy (when combined with microspectrophotometry) provided a level of discrimination not able to be achieved with microspectrophotometry as a single technique. Therefore, Raman spectroscopy should be considered when undertaking analysis of these sample types.

Keywords: Fibre evidence, Reactive Dyes, Raman Spectroscopy, Microspectrophotometry, Chemometrics